



Peculiar synergetic effect of MoS₂ quantum dots and graphene on Metal-Organic Frameworks for photocatalytic hydrogen evolution

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ARTICLE INFO

Article history:

Received 4 January 2017

Received in revised form 4 March 2017

Accepted 19 March 2017

Available online 23 March 2017

Keywords:

MoS₂ QDs

Metal-organic frameworks

Graphene

Photocatalytic hydrogen evolution

ABSTRACT

Special enhanced synergetic effect of MoS₂ quantum dots (MoS₂ QDs) and graphene on metal-organic frameworks for photocatalytic hydrogen evolution is obtained here. The photocatalytic activity of H₂ evolution reach 186.37 μmol over the EY-sensitized 5 wt% MoS₂ QDs/UiO-66-NH₂/G irradiated under visible light irradiation (λ ≥ 420 nm) in the first 3 h, and the apparent quantum efficiency (AQE) is 40.5% at 430 nm. The synergistic effect between MoS₂ QDs and graphene together with UiO-66-NH₂ is corroborated by photo-luminescence spectra, electro-chemical and photo-electro-chemical experiments. It demonstrate that the charge separation and the electrons transfer are more efficient with the aid of the MoS₂ QDs and graphene. MoS₂ QDs might be a potential photocatalyst for design new type of catalysts in photocatalysis proton reduction.

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1. Introduction

With a view to the growing concerns about global energy crisis and environmental issues, considerable efforts have been invested in clean energy sources to replace exhaustible fossil fuels. Hydrogen, with the fuel value (~143 kJ g⁻¹) three times higher than gasoline and only non-polluted water as by-product, is a possible candidate for future energy supplies [1–3]. Among various strategies for hydrogen evolution, the photocatalysis is considered as a most promising way, because it can direct utilization of solar energy to achieve H₂ generation from water splitting, as well as its potentially enables much simpler and more economically competitive systems [4]. Numerous efforts have carried out to develop efficient photocatalytic systems and photocatalysts over the past decades. However, up to now, the high cost noble metals remain dominantly as the most efficient co-catalysts [5]. Therefore, to develop low-cost non-noble-metal co-catalysts become an urgent task for advancing photocatalytic H₂ production.

Recently, the transition-metal dichalcogenide semiconductor molybdenum disulfide (MoS₂) has been regarded as a promising substitute for noble-metal co-catalysts in photocatalysis reactions [6–9]. The S-Mo-S coordination in the crystal lattices generates

unsaturated Mo and S atoms at the edge, leading to the unique “edges activity” of MoS₂ [2]. However, the limitation of active edges and the specific surface of MoS₂ have hindered the catalytic activity of MoS₂-based catalysts for efficient hydrogen evolution [2]. Therefore, MoS₂ had been fabricated into different structures to achieve higher catalytic activity for hydrogen evolution, such as nanoparticles, nanosheets, and monolayer or few layers. Among them, the higher quantum confinement and small-size effect of MoS₂ quantum dots (MoS₂ QDs) leads to unsaturated bond on surface and edges, proving more opportunity to connect with other atoms and obtain higher activity toward hydrogen evolution [1,2,10,11]. It is reported that MoS₂ QDs/Graphene/TiO₂ composite photocatalyst was fabricate by a simple one-pot solvothermal approach significant improved photocatalytic activity, which is caused by the increased charge separation, visible-light absorbance, specific surface area and reaction sites upon the introduction of MoS₂ QDs [12]. Others reported that MoS₂/WS₂ quantum dots rendered good HER catalytic activity, showing a small onset overpotential, along with long-term durability, because its larger concentration of active sites resulting from the unique monolayer and defect-rich nanostructures [13]. Recently, the monolayer MoS₂ QDs improved HER catalytic activities with a low overpotential of approximately 120 mV and a relatively small Tafel slope, owing its ultrathin structure and the abundance of exposed active edge sites, as well as the excellent intrinsic conductivity [14,15]. Moreover, MoS₂ QDs can gather the photoinduced electron around the edges and efficiently

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prevent charge recombination [2]. Therefore, MoS₂ QDs is a promising substitute for noble-metal co-catalysts toward photocatalytic hydrogen evolution.

Metal–organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials that are composed of clusters of a few metallic atoms held in a three-dimensional structure by organic linkers which have shown a variety of potential applications [16]. Especially, MOFs are attracting considerable attention as heterogeneous catalysts by introducing different types of catalytic sites into a porous MOF matrix over the past decade [17–19]. Recently, the utilization of MOFs for solar energy harvesting has been demonstrated, and MOFs are emerged as a new type of promising photocatalysts for water oxidation [17], photocatalytic CO₂ reduction [18,19], visible-light-driven photocatalytic organic reaction [16] and photocatalytic H₂ evolution [21]. Compared with the conventional photocatalysts, photoactive MOFs exhibited the highly porous structure with larger surface area, which facilitates the mass transport in photocatalytic reactions [22]. Under light illumination, organic linkers as photon antennas will be excited to generate electrons and holes, which is the essential process for photocatalytic reactions. Moreover, the controllable chemical and physical properties could be easily realized by tuning the organic functionalities and metal center at the molecular level [23]. Garcia and co-workers used a water stable Zr-containing MOFs of UiO-66 and UiO-66(NH₂) as a photocatalyst for water splitting under UV light irradiation, which opened the door for MOFs to photocatalytic hydrogen evolution from water splitting [21]. However, the MOFs suffered from poor photoactivity, because they cannot respond to visible-light effectively. To extend the photo-response and photo-activity of MOFs, Pt nanoparticles or organometallic compounds have been incorporated into the MOFs to build catalytic-active-sites for hydrogen evolution. For example, Fateeva et al. reported a visible-light-response porphyrin-based MOFs photocatalyst for photocatalytic hydrogen production, which can be attributed to the porphyrins that are versatile functional molecules in catalysis, light harvesting, and molecular sensing [24]. Very Recently, the MoS₂ and CdS nanoparticles decorated on MOFs enhanced photocatalytic activity for hydrogen production under visible light irradiation [25,26]. Dye-sensitization has become a relatively mature technology in solar dye sensitized solar cell for visible-light harvesting and also applied in photocatalysis. The photocatalytic activity of for hydrogen evolution of UiO-66(Zr) were extremely enhanced by means of sensitization with Rhodamine B dye [27]. Most recently, the Erythrosin B dye to sensitize Zr-containing MOFs of UiO-66 also exhibits highly photocatalytic activity for H₂ production [23]. Both MOFs and dyes containing benzene ring, it is expected that a strong π - π stacking and Van Der Waals interaction between MOFs and dyes, which is very important for efficient electron transfer in dye-sensitized photocatalytic system [23]. In addition, the metal centers separated by organic linkers in MOFs can serve as “quantum dots”, therefore the short transport length of charge carriers can be achieved in MOFs. What's more, water molecules can easily diffuse into the pores of MOFs, thus making proton H reduction in MOFs as “quasi-homogeneous reaction” [23]. The above-mentioned advantages make dye-sensitized MOFs as potential active photocatalysts for hydrogen production from water reduction.

Graphene was a well-known co-catalyst for efficient photocatalytic H₂ evolution due to its high specific surface area and superior electron mobility [28]. In this work, metal–organic frameworks UiO-66-NH₂ grown on graphene (UiO-66-NH₂/G) by *in situ* solvothermal was employed as a photocatalyst decorating MoS₂ QDs (MoS₂ QDs/UiO-66-NH₂/G) for efficient photocatalytic hydrogen production. MoS₂ QDs and graphene as dual co-catalysts with the strong light harvesting of EY-sensitized UiO-66-NH₂ and efficient electron extraction effect of graphene, can efficiently produce H₂ from water splitting. MoS₂ QDs with small size exhibit stronger

quantum confinement, higher specific surface area and more edge atoms, resulting in a lack of coordination of the surface atoms and increase in unsaturated bonds [1]. Therefore, these unstable atoms have high surface activity and it is easy to combine with other atoms. Meanwhile, this surface effect offers unique electrical/optical properties, which in favor of the catalytic activity for hydrogen evolution [1]. Moreover, a high apparent quantum yields (AQEs) of 40.5% at 430 nm and a robust photocatalytic activity for H₂ evolution under visible light irradiation were achieved. Additionally, MoS₂ QDs/UiO-66-NH₂/G exhibited a better stability for hydrogen production under constant illumination. Interestingly, it was found that the combination of MoS₂ QDs and graphene together with UiO-66-NH₂ offered synergetic effects that lead to special reaction pathways which was not seen in MoS₂ QDs or graphene alone.

2. Experimental section

2.1. Preparation of photocatalysts

All reagents were analytical grade and used without further purification.

2.1.1. Synthesis of graphene oxide

Graphene oxide (G) was synthesized via the same procedure as our previous work [29]. All the reagents were of analytical grade and were used without further purification. In short, 20 g of graphite powder and 10 g of NaNO₃ were mixed together, followed the mixture was added to cold concentrated H₂SO₄ (0 °C, 460 mL) under constant stirring. After 1 h, 60 g of KMnO₄ was gradually added to the above solution while keeping the temperature less than 20 °C to prevent overheating and explosion. The mixture was then stirred at 35 °C for 2 h and the resulting solution was diluted with 920 mL of water under vigorous stirring for 15 min. The reaction was terminated by adding distilled water (2.8 L) and then H₂O₂ solution (50 mL, 30%). The product was filtered, washed repeatedly with HCl solution (1:10, v/v) until sulfate could not be detected with BaCl₂, and then dried in a vacuum oven at 40 °C for 24 h.

2.1.2. Synthesis of UiO-66-NH₂

UiO-66-NH₂ was synthesized via solvothermal route [30]. In a typical synthesis, ZrCl₄ (0.2332 g, 1.0 mmol) and 2-NH₂-benzenedicarboxylate (0.1812 g, 1.0 mmol) were dissolved in 50 mL N,N-Dimethylformamide (DMF), and then the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated in an oven at 120 °C for 48 h. After cooled naturally, the product was collected by centrifugation and washed for three times with DMF, and then sequentially purified within methanol for several times to make sure that the occluded DMF molecules were eliminated, followed by drying under vacuum (100 °C 12 h) before using the samples for the photocatalytic reactions.

2.1.3. Synthesis of UiO-66-NH₂/G

The synthesis route of UiO-66-NH₂/G was similar to UiO-66-NH₂. Typically, 10 mg GO was dispersed in 50 mL DMF by ultrasonication to form a homogeneous solution. ZrCl₄ (0.2332 g, 1.0 mmol) and 2-NH₂-benzenedicarboxylate (0.1812 g, 1.0 mmol) were dissolved in the homogeneous solution. After magnetic stirring for 30 min, the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, and allowed to react following the same steps as mentioned above.

2.1.4. Synthesis of MoS₂ QDs

MoS₂ QDs was synthesized by a surfactant-assisted ultrasonic exfoliated bulk MoS₂ [1,31]. Typically, 400 mg bulk MoS₂ powder

was dispersed in 20 mL of N-methylpyrrolidone (NMP) to form a black solution, followed by ultrasonication for three hours at a power of 300 W in an ice-bath. After that, 0.05 M sodium hydroxide (NaOH) was added into solution followed by ultrasonication for another two hours in ice-bath. Then, the solution was first centrifuged at 7000 rpm for 30 min. The supernatant was filtered several times using a 0.22 μm organic microporous membrane. The filtrate was added to hexane and chloroform (NMP: hexane: chloroform = 1: 1:1, v/v/v), and the product was collected by centrifugation at 8000 rpm for 10 min [31]. And then the product was dispersed in deionized water (the concentration is 3 mg/mL) for further used.

2.1.5. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtered Cu K α radiation operated at 40 kV and 30 mA. Field emission scanning electron microscopy (FESEM) images were recorded on a JSM-6701F scanning electron microscope operated at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on K-Alpha-surface Analysis (Thermo Scientific) using X-ray monochromatization. The nitrogen adsorption–desorption isotherms of samples were measured at 77 K with an ASAP 2020 M instrument and analyzed by the Brunauer-Emmett-Teller (BET) equation. The pore size distribution plots were obtained by the Barret-Joyner-Halenda (BJH) model. UV/Vis absorption spectra were taken at room temperature on a UV-2550 (Shimadzu) spectrometer. Photoluminescence data (PL) were acquired using a FLUOROMAX-4 spectrophotometer at room temperature.

2.1.6. Photocatalytic H₂ evolution experiments

Photocatalytic experiments were conducted in a one-compartment Pyrex reactor *ca.* 178 cm³ having a flat window *ca.* 10.2 cm² for illumination. In a typical photocatalytic experiment, 30 mg of catalyst was suspended in 100 mL 10% (v/v) triethanolamine (TEOA) aqueous solution contain a certain amount of MoS₂ QDs and 28 mg dye Eosin Y (EY) (4×10^{-4} M) by means of ultrasonication for about 10 min. The opening of the reactor was sealed with a silicone rubber septum. The reactant mixture was degassed by bubbling N₂ gas for 40 min to remove air and ensure that the reaction system was under anaerobic conditions, and then was irradiated by a 300-W Xe lamp with a cutoff filter of 420 nm for H₂ evolution under magnetic stirring condition. The amount of hydrogen evolution was measured using gas chromatography (Tianmei GC7900, TCD, 13X column, N₂ as carrier).

The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction conditions with irradiation light through a bandpass filter (430, 460, 490, 520, or 550 nm) [32]. Photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400–700 nm; sensitivity, 10–50 $\mu\text{V} \mu\text{mol}^{-1} \text{m}^{-2} \text{s}^{-1}$). The reaction solutions were irradiated for 30 min with bandpass filters for AQE tests on the H₂ production. The following equation was used to calculate the AQE.

$$\text{AQE} = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\% \quad (1)$$

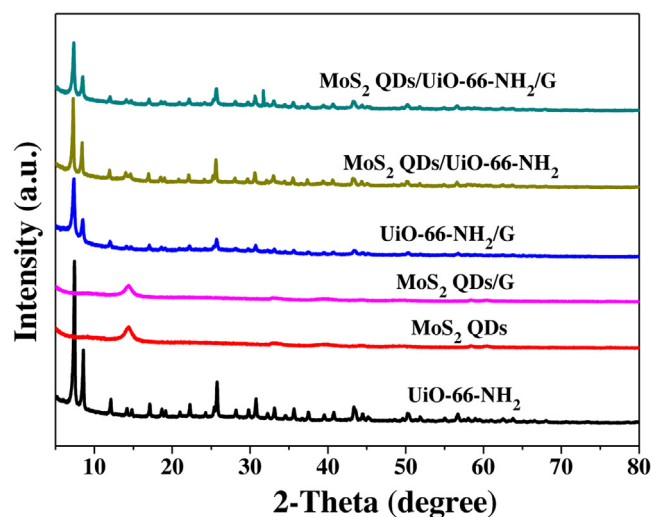


Fig. 1. XRD patterns of UiO-66-NH₂, MoS₂ QDs, MoS₂ QDs/G, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂ and MoS₂ QDs/UiO-66-NH₂/G composites.

The turnover number (TON) and turnover frequency (TOF) of dye Eosin Y for H₂ evolution are calculated by using the following equations [33]:

$$\text{TON} = \frac{2 \times \text{number of evolved hydrogen molecules}}{\text{number of dye Eosin Y molecules}} \quad (2)$$

2.1.7. Photoelectrochemical measurements

The photoelectrochemical measurement was performed on an electrochemical analyzer (Chenhua CHI 660D) in a standard three-electrode cell [29]. The working electrodes were prepared by drop-coating homogeneous catalyst suspensions directly onto the precleaned indium tin oxide glass (FTO glass) surfaces (1 × 2 cm), and then 500 μL of EY aqueous solution (4.0×10^{-4} mol L⁻¹) was added onto the above catalyst film electrode surface and then dried at 100 °C for 1 h. Platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte was 10 v/v% TEOA (pH 7) mixed with 0.1 mol L⁻¹ Na₂SO₄ aqueous solution. The surface area of the working electrode exposed to the electrolyte was about 0.95 cm². A 300-W Xe lamp equipped with an optical cutoff filter of 420 nm was employed for the visible-light excitation. EIS Nyquist plots were collected at open circuit potential, with the frequency ranging from 100 kHz to 0.01 Hz and the modulation amplitude of 5 mV.

3. Results and discussion

3.1. Characterization supports of catalysts

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of the UiO-66-NH₂, MoS₂ QDs, MoS₂ QDs/G, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂ and MoS₂ QDs/UiO-66-NH₂/G nanocomposites to certify the phase structure. It can be seen that the as-prepared UiO-66-NH₂, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂ and MoS₂ QDs/UiO-66-NH₂/G nanocomposites have the similar XRD patterns. No obvious shift in the peaks of UiO-66-NH₂ is obvious in the UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂ and MoS₂ QDs/UiO-66-NH₂/G samples, suggesting that integrity of UiO-66-NH₂ is maintained which not is influenced by graphene and MoS₂ QDs. The sharp peaks of UiO-66-NH₂ indicate its excellent crystallinity, and all the peak can well matched with the reported results [19,30]. MoS₂ QDs and MoS₂ QDs/G samples also have the similar XRD patterns, one small peak at 14.37° belong to (002) plane which fit well with MoS₂ (JCPDS# 77-1716)

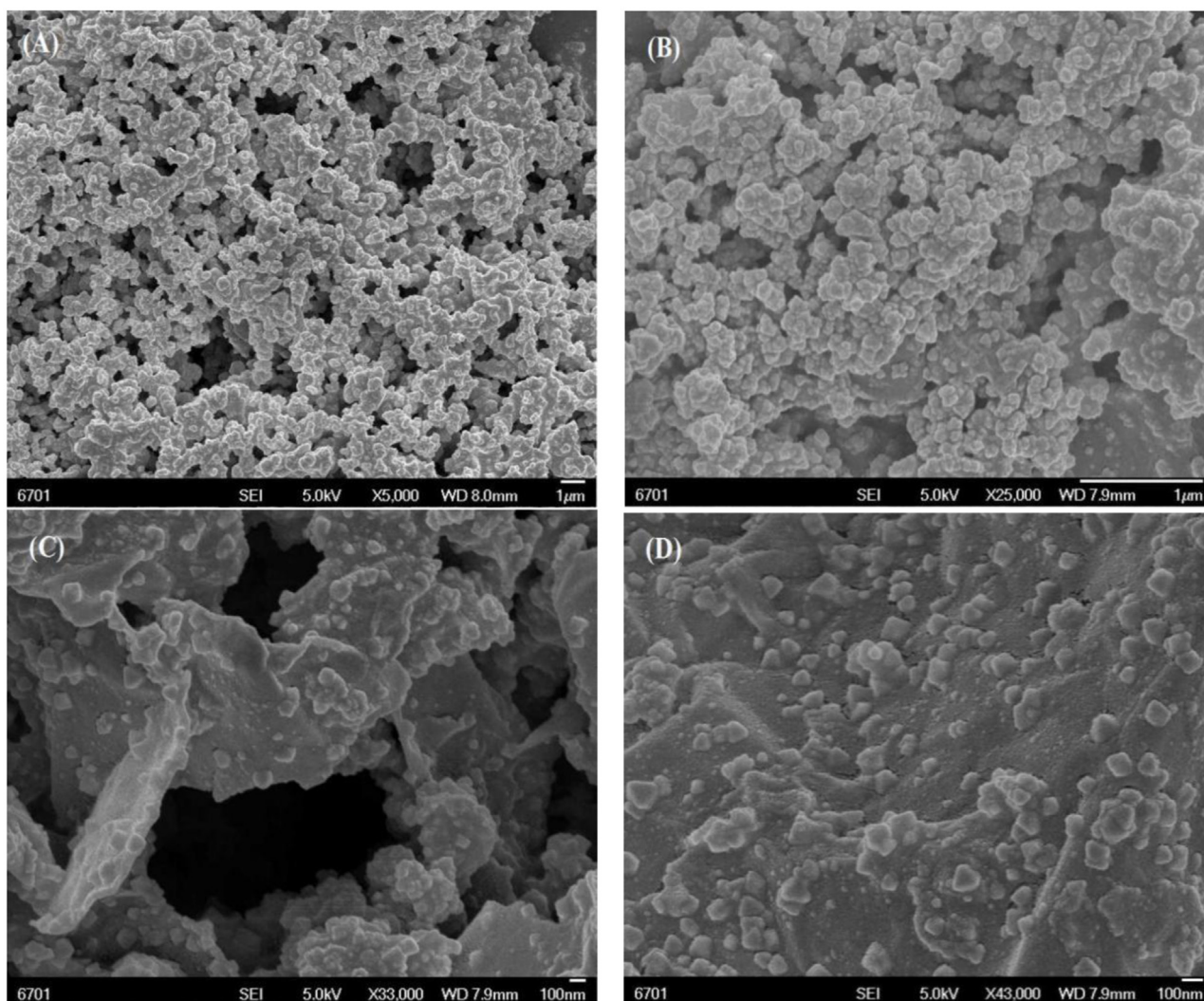


Fig. 2. SEM images of (A) UiO-66-NH₂; (B) UiO-66-NH₂/G; and (C–D) 5 wt% MoS₂ QDs/UiO-66-NH₂/G composites.

can be observed. For the MoS₂ QDs/G and UiO-66-NH₂/G samples, the peak belong to graphene is not observed. As for the sample of MoS₂ QDs/UiO-66-NH₂/G, the peaks of MoS₂ QDs and graphene is not appear, only the XRD pattern of UiO-66-NH₂ is observed. The possible reason is that the content of MoS₂ QDs too small to examine. It can be concluded that the MoS₂ QDs and graphene have not destroyed the structure of UiO-66-NH₂.

3.1.2. SEM characterization

The morphologies of UiO-66-NH₂, UiO-66-NH₂/G and MoS₂ QDs/UiO-66-NH₂/G nanocomposites were examined by SEM. The pure UiO-66-NH₂ (Fig. 2A) is prone to multi-stacking porous structures of irregular nanoparticles, many hollow structures can be observed on the surface. The UiO-66-NH₂/G (Fig. 2B) is also presented as the similar porous structure to the UiO-66-NH₂, but the irregular nanoparticles is more bigger. From Fig. 2C, it can be see that UiO-66-NH₂ nanoparticles decorated on the surface of graphene sheets. The some rhombus-like and irregular particles are decorated on the surface of graphene sheets in the composite of MoS₂ QDs/UiO-66-NH₂/G (Fig. 2D), and they appear to uniform distribution which have a diameter of 5–100 nm. Furthermore, the MoS₂ QDs is not clearly observed on the surface of UiO-66-NH₂/G, it will further characterization by TEM.

3.1.3. TEM characterization

The TEM images of the UiO-66-NH₂/G nanocomposite revealed that a large amount of rhombus-like nanoparticles of UiO-66-NH₂ grown on the surface of graphene sheets in Fig. 3A, which is agreement with the SEM images results of Fig. 2C and D. Fig. 3B and C clearly indicate that the increasing introduction of MoS₂ QDs led to the agglomeration of MoS₂ QDs on the surface of UiO-66-NH₂/G in the composite of MoS₂ QDs/UiO-66-NH₂/G. The energy dispersive X-ray (EDX) results further confirm the co-existence of C, N, Zr, Mo and S elements in the area of red square of the MoS₂ QDs/UiO-66-NH₂/G nanohybrid (Fig. 3D), which was supported by the XPS results of MoS₂ QDs/UiO-66-NH₂/G.

3.1.4. X-ray photoelectron spectroscopy (XPS)

With a view to further ascertain the details of the chemical composition and elemental states of 5 wt% MoS₂ QDs/UiO-66-NH₂/G, XPS measurements were carried out. The XPS survey spectrum, as presented in Fig. 4A, revealing that the catalyst mainly consist of Zr, C, N, Mo, S, and O elements, which in agreement with the EDX results. In Fig. 4B, the curve of Zr 3d region could be deconvoluted into two peaks for Zr 3d_{5/2} and Zr 3d_{3/2} located at around 182.20 eV and 184.70 eV, respectively [30]. In Fig. 4C, two single peaks at 395.14 eV and 399.68 eV can be observed for N 1s XPS spectrum. The former peak could be attributed to the N atoms of NH₂ groups bonded with carbon atoms of graphene in the sample, whereas the

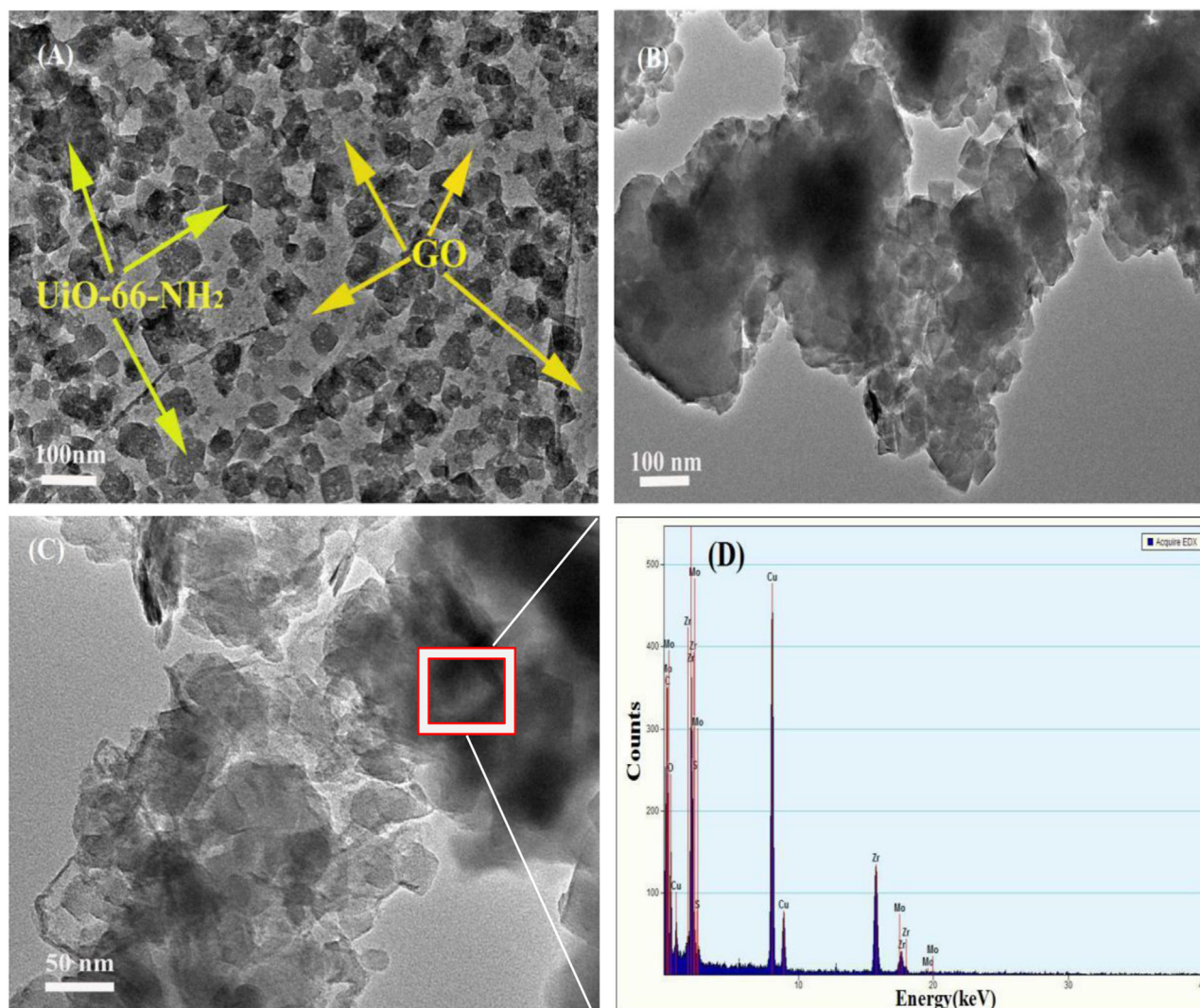


Fig. 3. TEM images of (A) UiO-66-NH₂/G and (B–C) 5 wt% MoS₂ QDs/UiO-66-NH₂/G composites; (D) EDX spectrum of 5 wt% MoS₂ QDs/UiO-66-NH₂/G in which the Cu signals originated from the Cu grid support for the TEM observation.

latter peak could be assigned to the retained organic linkers-NH₂ groups which do not bond with carbon atoms of graphene after the hydrothermal processing. In Fig. 4D, the C 1s can be deconvoluted into three peaks, the peak located at 284.85 can be assigned to carbon sp² in phenyl for the catalyst or the amorphous. The peak at 286.58 eV could be attributed to the C–O in the graphene sheets, and the peak at 288.84 eV, which represent the C–N–H and C–N–C functional groups in the MoS₂ QDs/UiO-66-NH₂/G structure. The Mo 3d spectrum in Fig. 4E shows the binding energy of Mo 3d_{3/2} (232.43 eV) and Mo 3d_{5/2} (229.2 eV) indicated that Mo was in the form of Mo⁴⁺ in MoS₂ QDs. The peak at 235.62 eV is attributed to Mo⁶⁺ in MoO₃. In Fig. 4F, the peak at 162.06 eV is ascribed to S 2p_{3/2}, while the peak at 163.23 eV could be assigned to S 2p_{1/2}. The other peak at around 169.31 eV could be attributed to the SO₄^{2–} species, which maybe originate from the MoS₂ during photocatalytic processing. Both the high resolution spectra of Mo 3d and S 2p ascertain the existence of MoS₂ QDs in the composite.

3.1.5. UV–vis diffuse reflectance spectra

The optical property of MoS₂ QDs/UiO-66-NH₂/G composite was investigated using UV–vis diffuse reflectance spectroscopy. All the samples absorb UV to visible light as expected (Fig. 5), which signifies their visible-light-induced photocatalytic activity. The pure

UiO-66-NH₂ sample shows an absorption edge of ~435 nm corresponding to a band gap of 2.78 eV. The absorption onset of the MoS₂ QDs is at 461 nm, corresponding to a band gap of 1.69 eV. The excitonic peak at 660 nm deriving from the K point of the Brillouin zone of MoS₂, which can be distinctly observed both in the composites and in MoS₂ QDs, revealing MoS₂ QDs has been successfully decorated on the surface of UiO-66-NH₂/G [2]. Compared with pure UiO-66-NH₂ and MoS₂ QDs, the MoS₂ QDs/UiO-66-NH₂/G composite shows a much stronger absorption within the visible light range and a red shift appears upon the addition of MoS₂ QDs and graphene, as well as the intensity increases.

3.1.6. Brunauer–Emmett–Teller (BET) nitrogen adsorption isotherm characterization

In order to analyze the textural properties of these samples, the BET surface area and the corresponding curves of the pore size distributions for the samples are investigated using nitrogen adsorption–desorption isotherms measurements at 77 K. The pore size distributions were determined using desorption data by the Barrett–Joyner–Halenda (BJH) method. For the UiO-66-NH₂, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂/G samples, the curves are type IV isotherms with H3 typical hysteresis loop, as observed in Fig. 6A. At the high relative pressure (P/P₀) they show high

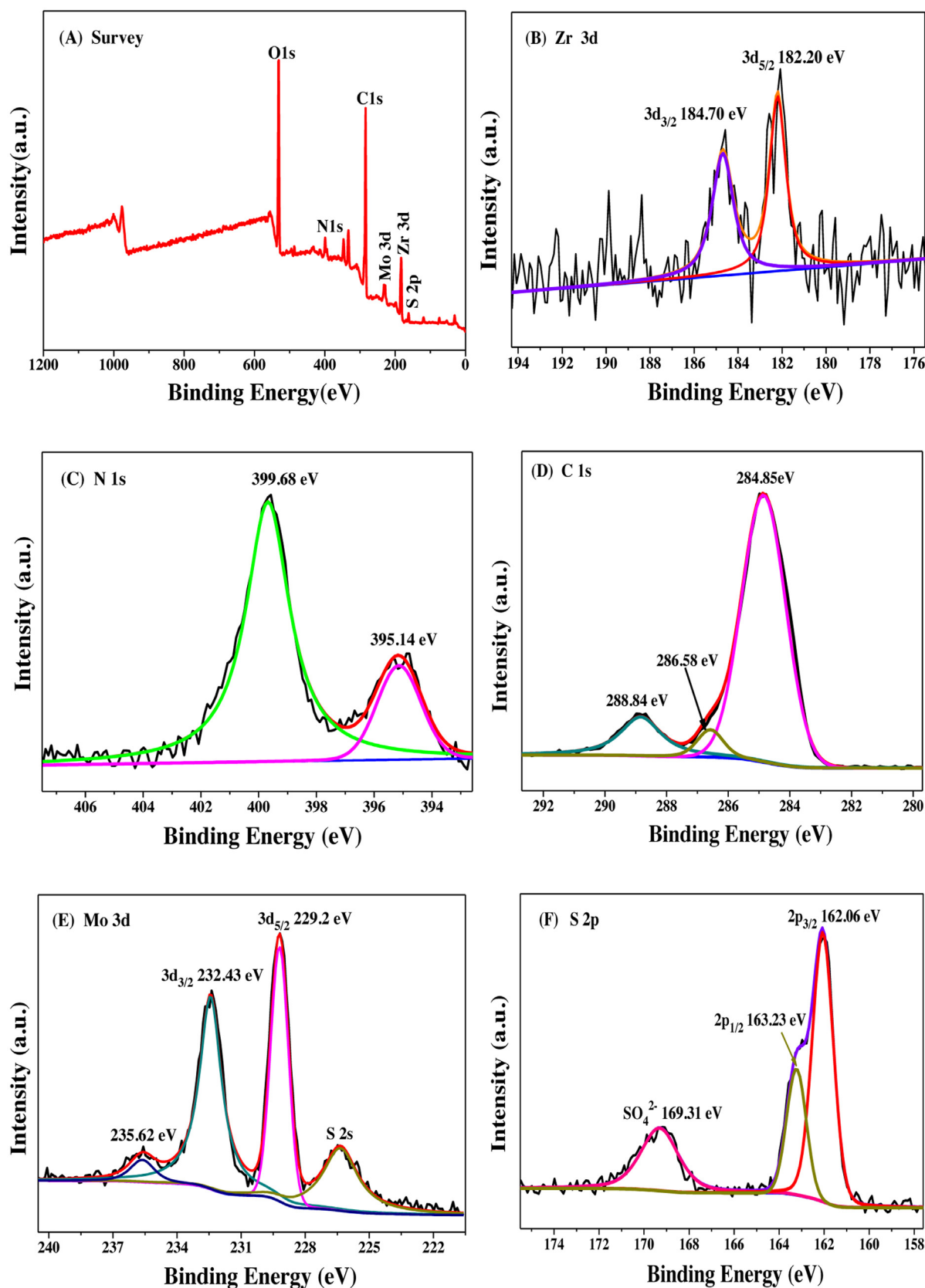
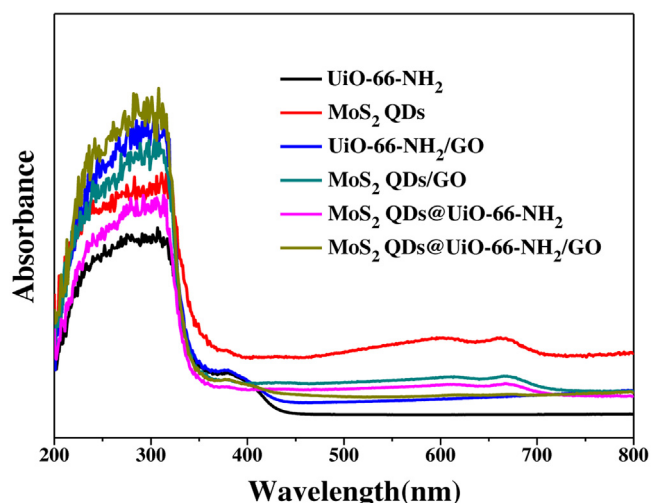


Fig. 4. XPS patterns of 5 wt% MoS₂ QDs/UiO-66-NH₂/G sample. (A) Survey spectra, (B) Zr 3d, (C) N 1s, (D) C 1s, (E) Mo 3d and (F) S 2p scan spectra of the MoS₂ QDs/UiO-66-NH₂/G sample.

Table 1Structural parameters obtained from N₂ adsorption isotherms analysis.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^{a)}	Pore volume ($\text{cm}^3 \text{g}^{-1}$) ^{b)}	Average pore size (nm) ^{b)}
UiO-66-NH ₂	712.33	0.35	2.04
UiO-66-NH ₂ /G	557.78	0.34	2.55
MoS ₂ QDs/UiO-66-NH ₂ /G	457.24	0.29	2.46

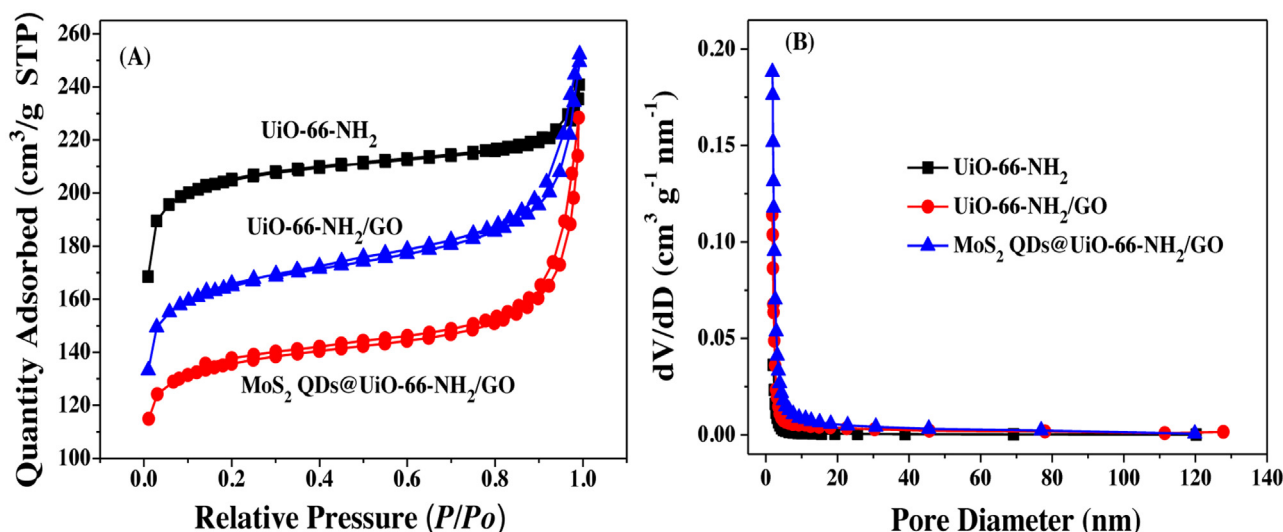
^{a)}Obtained from BET method;^{b)}Total pore volume taken from the N₂ adsorption volume at a relative pressure (P/P_0) of 0.97.**Fig. 5.** UV-vis diffuses reflectance spectra of UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs/UiO-66-NH₂, MoS₂ QDs/UiO-66-NH₂/G samples.

adsorption, indicating the presence of accumulative pores [20]. The S_{BET} of UiO-66-NH₂, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂/G were 712.33, 557.78 and 457.24 $\text{m}^2 \text{g}^{-1}$, respectively. The S_{BET} of UiO-66-NH₂ sample (712.33 $\text{m}^2 \text{g}^{-1}$) gradually dwindle after add graphene (557.78 $\text{m}^2 \text{g}^{-1}$) and MoS₂ QDs (457.24 $\text{m}^2 \text{g}^{-1}$), which indicating graphene and MoS₂ QDs have a marked influence to the S_{BET} of samples. The pore size distributions curves in Fig. 6B show that porous UiO-66-NH₂, UiO-66-NH₂/G, MoS₂ QDs/UiO-66-NH₂/G display a similar curves, which mainly consist of large size pores. For all of these samples show a mesoporous structure, which are confirmed by the corresponding pore size distribution as shown in Table 1. Meanwhile, Compared to the UiO-66-NH₂/G, the MoS₂

QDs/UiO-66-NH₂/G has a smaller pore volume (0.29 $\text{cm}^3 \text{g}^{-1}$) and pore size (2.46 nm), which suggesting that the introduced MoS₂ QDs maybe get into the porous structures and channels of MOF result in the reduce of pore volume and pore size. This is maybe more conducive to the catalytic reaction.

3.2. Photocatalytic activities over Eosin Y-sensitized MoS₂ QDs/UiO-66-NH₂/G for H₂ evolution

The photocatalytic activities of the catalysts were evaluated using TEOA as sacrificial donor under visible light irradiation ($\lambda \geq 420 \text{ nm}$). As shown in Fig. 7, the presence of MoS₂ QDs and graphene were crucial for improving the photocatalytic H₂ evolution activity. The amount of H₂ over EY-sensitized UiO-66-NH₂ generated only 1.07 μmol which increased a little after decorated on the graphene (1.98 μmol), suggesting that the UiO-66-NH₂ itself was inactive for H₂ evolution probably due to its cannot absorb visible light. For the MoS₂ QDs, there 37.62 μmol H₂ was produced after 3 h irradiation. When introduction of the graphene, the photocatalytic activity reached 63.09 μmol , which indicating the synergetic effect existence between MoS₂ QDs and graphene. Very interestingly, the H₂ evolution of MoS₂ QDs/UiO-66-NH₂ reached 75.1 μmol , which was more active than the MoS₂ QDs/G. It was maybe existed the formation of the synergetic effect between MoS₂ QDs and UiO-66-NH₂ for hydrogen evolution. These results shown that MoS₂ QDs can as a photocatalyst and co-catalyst for photocatalytic H₂ production effectively under visible light. Thereby, for MoS₂ QDs/UiO-66-NH₂/G, the H₂ generation rate reached 186.37 μmol , which was significantly increased as expected, owing to the quantum confinement effect of MoS₂ QDs can help in the charge separation, and the synergetic effect of MoS₂ QDs and graphene together with UiO-66-NH₂ for electron transfer, thus enhancing the photocatalytic H₂ evolution activity. In this particular instance, MoS₂ QDs introduce active sites, graphene as electron

**Fig. 6.** (A) BET adsorption – desorption isotherms of catalysts and (B) the corresponding pore size distributions.

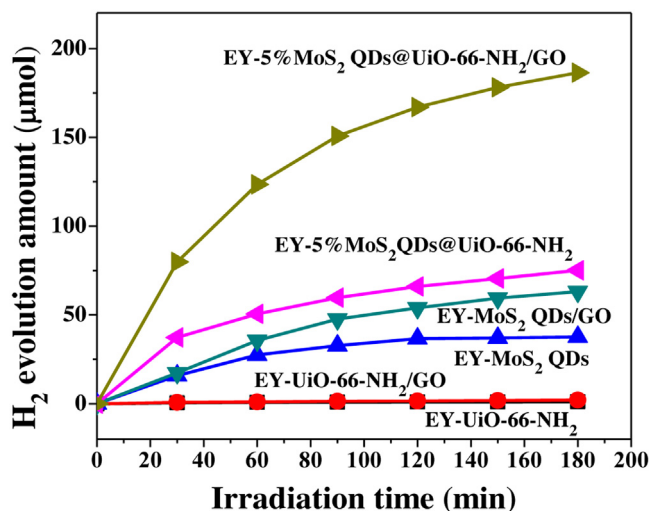


Fig. 7. The photocatalytic activities of the EY-sensitized (4.0×10^{-4} mol L⁻¹) photocatalysts in 100 mL 10 v/v% TEOA aqueous solution (pH 7) for hydrogen evolution under visible light irradiation ($\lambda \geq 420$ nm).

transfer medium required for efficient H₂ production in combination with the light absorbing unit, EY. The turnover number (TON) of dye Eosin Y for H₂ evolution is calculated with the equation [2]. Here, the moles of dye Eosin Y is 4×10^{-5} in the reaction solution and the amount of production H₂ is 186.37 μmol in first 3 h over EY-5 wt% MoS₂ QDs/UiO-66-NH₂/G photocatalyst. Therefore, the calculated TON is 9.32 of dye Eosin Y in the first 3 h for photocatalytic H₂ evolution.

3.3. Effect of the pH and the MoS₂ QDs ratio on the photocatalytic activity of MoS₂ QDs/UiO-66-NH₂/G

It was known that the solution pH had a significant influence on photocatalytic activity [29]. As shown in Fig. 8A, acidic and strongly alkaline conditions are not conducive to H₂ production. When pH values of TEOA aqueous solution varied from 5 to 9, the rate of photocatalytic hydrogen generation maximized at pH 7 (62.12 μmol h⁻¹). The likely reason for the decrease rate of hydrogen evolution was that the state of TEOA which was affected by the pH of the solution. At acidic pH, more H⁺ results in protonation of TEOA, which was a less effective electron donor, thus leading to a shorter lifetime of the excited EY and lower efficiency of the excited dye species [28]. Under basic condition, the thermodynamic driving force for hydrogen evolution from water decreased due to the lower concentration of H⁺ [34]. Moreover, the adsorption behavior of EY onto the frameworks of UiO-66-NH₂ also be affected by the pH. The photocatalytic results indicated the dye can be effectively absorbed on the UiO-66-NH₂ at pH 7 and EY can be reductively quenched by TEOA absolutely at this pH 9.

In addition, we further investigated the influence of different content of MoS₂ QDs loading to UiO-66-NH₂/G on the photocatalytic hydrogen evolution activity, and a significant impact from the MoS₂ QDs content was found. Fig. 8B emphasizes that the MoS₂ QDs content is pivotal for optimal photocatalytic activity. At zero content, the UiO-66-NH₂/G composite shown a tiny photocatalytic activity with a H₂ generation rate of 0.66 μmol h⁻¹. The photocatalytic hydrogen production increased with a rise in MoS₂ QDs content. When a small amount of MoS₂ QDs (1 wt %) introduced into the composite, the photocatalytic activity was enhanced to 9.71 μmol h⁻¹, which is 14.5 times greater than that of the bare UiO-66-NH₂/G. It is speculated that the quantum confinement effect of MoS₂ QDs is beneficial to the charge separation and improve the photocatalytic activity as well. When the MoS₂ QDs content

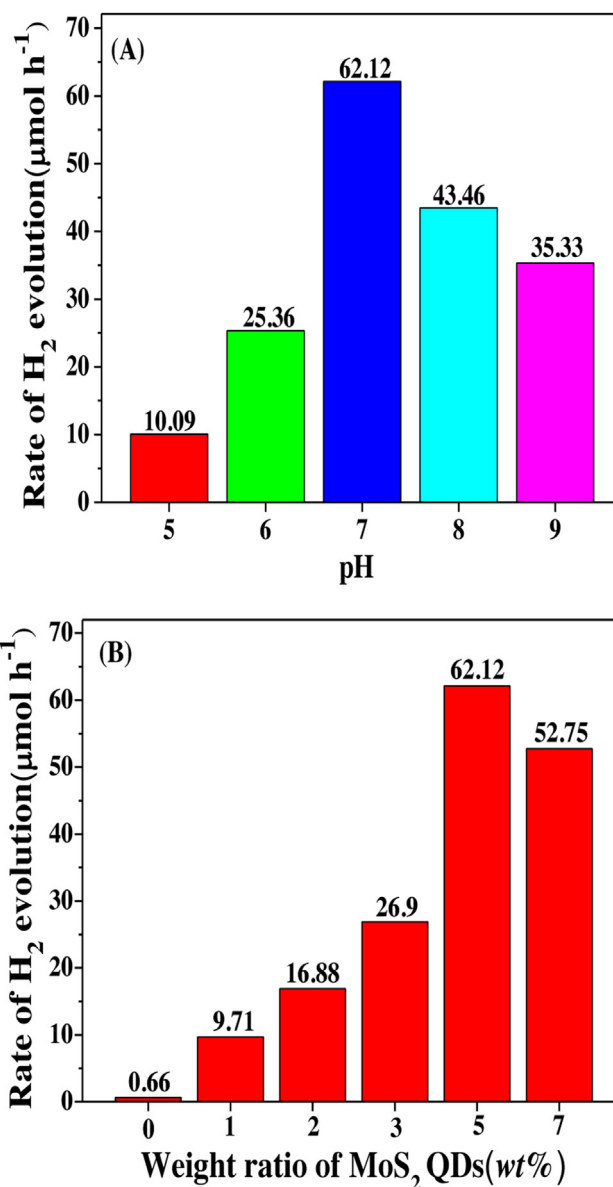


Fig. 8. (A) Effect of the pH on the photocatalytic activity of MoS₂ QDs/UiO-66-NH₂/G for hydrogen evolution and (B) effect of the different MoS₂ QDs mass ratios from 1 to 7 on the photocatalytic activity of MoS₂ QDs/UiO-66-NH₂/G in 10% (v/v) TEOA aqueous solution (pH 7) under visible light irradiation.

up to 5 wt %, the H₂ produced rate achieved a maximum value of 62.12 μmol h⁻¹, which is 94.1 times higher than that of the UiO-66-NH₂/G. Here, the turnover number (TON) of dye Eosin Y and MoS₂ QDs for H₂ evolution is 9.3 and 39.8 in the first 3 h, respectively. [Corresponding to an apparent quantum efficiency (AQE) of 40.5% at 430 nm]. And further increases in the MoS₂ QDs content in the catalyst led to a downward photocatalytic activity. This maybe a higher MoS₂ QDs content is agglomeration on the UiO-66-NH₂/G that not in favor of the charge separation and the migration of photogenerated electrons.

3.4. Apparent quantum efficiencies (AQEs) and stability tests

The wavelength dependence of photocatalytic H₂ evolution was investigated over a wide visible light range of 430–550 nm [32], and the apparent quantum efficiencies (AQEs) of EY sensitized 5 wt% MoS₂ QDs/UiO-66-NH₂/G for H₂ evolution were calculated by the

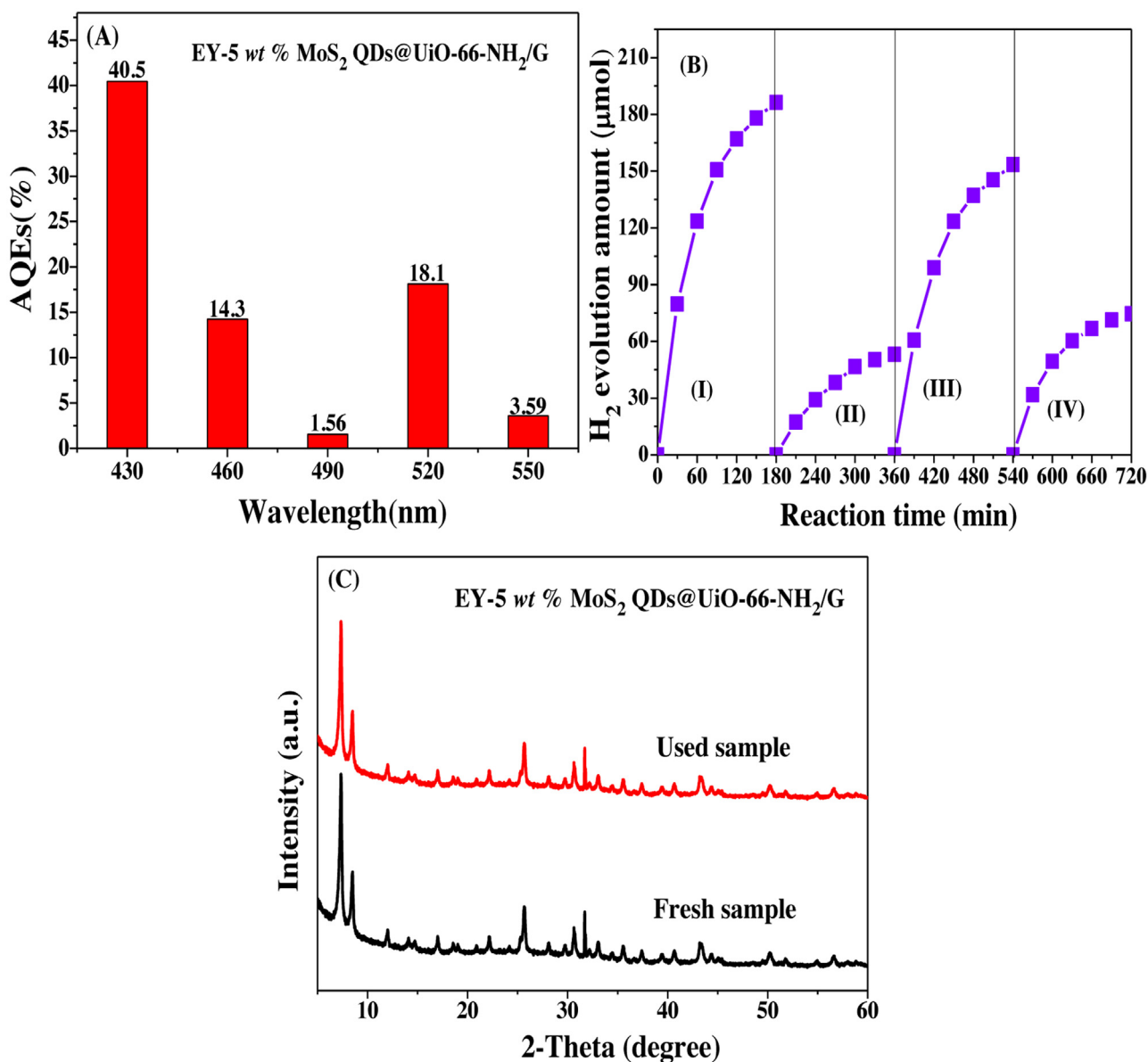


Fig. 9. Apparent quantum yields (AQEs) of hydrogen evolution for EY ($4.0 \times 10^{-4} \text{ mol L}^{-1}$) sensitized 5% MoS₂ QDs@UiO-66-NH₂/G in 100 mL of 10 v/v% TEOA-H₂O solution (pH 7) under different wavelength irradiation (reaction time: 30 min); (B) Stability test of EY sensitized 5 wt% MoS₂ QDs@UiO-66-NH₂/G for H₂ generation under visible light irradiation in TEOA-H₂O solution (pH 7). The reaction was continued for 720 min, with evacuation every 120 min. (I) First run; (II) evacuation; (III) add EY and TEOA, repeat II; (IV) repeat III. (C) The XRD patterns of before and after stability test of 5 wt % MoS₂ QDs@UiO-66-NH₂/G.

corresponding formula. As shown in Fig. 9A, it can be observed that the AQEs decreases with increasing wavelengths and the highest AQEs was 40.5% at 430 nm. Interestingly, another high AQE was achieved at 520 nm, which was related to the highest absorption wavelength of EY (518 nm) [32]. These results suggested that the H₂ production reaction was indeed driven with the absorbing unit, EY.

The stability test of 5 wt% MoS₂ QDs@UiO-66-NH₂/G was investigated over four runs of totally 720 min, and the results were shown in Fig. 9B. It was observed that in the first run, the maximum amounts of photocatalytic H₂ evolution was 186.37 μmol. But in the second run, the amounts of photocatalytic H₂ evolution sharply declined. The H₂ evolution activity of MoS₂ QDs@UiO-66-NH₂/G could be revived by the concurrent addition of EY and TEOA in the third run. The reason is that the stability of the dye sensitizer is not good because of the adsorbed EY dye is easy to be desorbed and diffuse into the solution, and it could be decomposed

under light irradiation [25]. Whereas the XRD patterns of the fresh and used EY sensitized 5 wt% MoS₂ QDs@UiO-66-NH₂/G (Fig. 9C) are almost the same, implying that MoS₂ QDs@UiO-66-NH₂/G is stable under light irradiation.

3.5. Photoluminescence (PL) analysis

To prove the important role of MoS₂ QDs and graphene in facilitating the transfer of photogenerated electrons, the photoluminescence quenching of EY in the presence of the UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs@UiO-66-NH₂ and MoS₂ QDs@UiO-66-NH₂/G were further performed. As shown in Fig. 10, EY solution ($1 \times 10^{-6} \text{ mol L}^{-1}$) excited at 480 nm shows a typically extensive emission peak at 539 nm. When the pure UiO-66-NH₂ was added, a slight decline occurred. As MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, and MoS₂ QDs@UiO-66-NH₂ were introduced into the EY aqueous solution, a significant decrease was

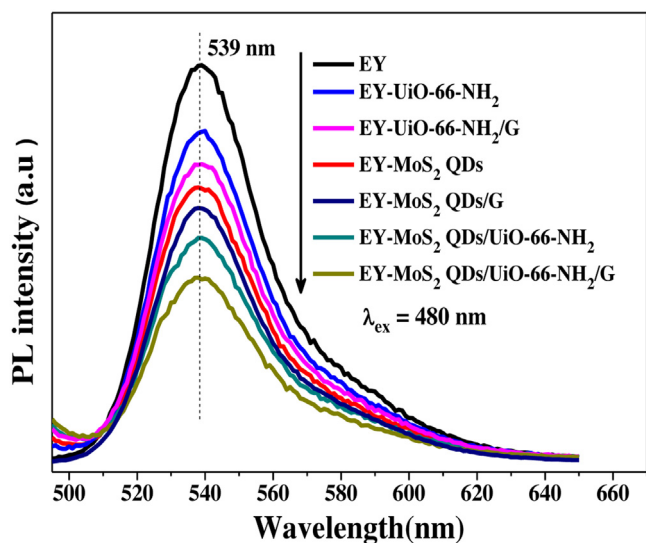


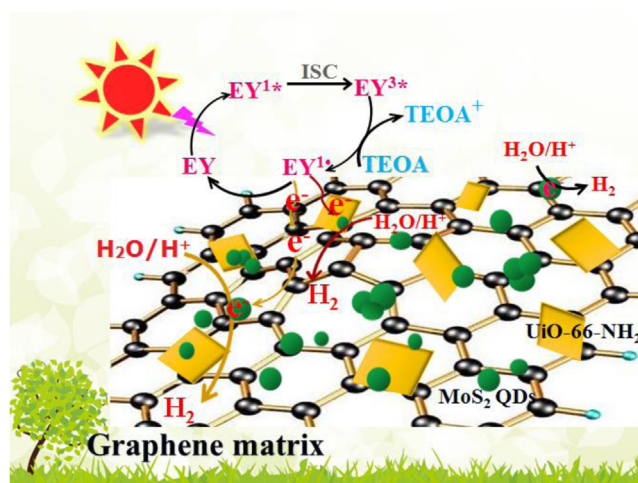
Fig. 10. Fluorescence spectra of the EY-sensitized UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs/UiO-66-NH₂, MoS₂ QDs/UiO-66-NH₂/G in 10 v/v% TEOA aqueous solution at pH 7. [Catalysts]: 0.15 mg mL⁻¹.

observed at the emission wavelength of 539 nm, it can be attributed to graphene or MoS₂ QDs which is believed to promote the migration of photo-generated electrons. And we can observe the photoluminescence dropped markedly when MoS₂ QDs/UiO-66-NH₂/G was introduced, indicating the synergistic effect of MoS₂ QDs and UiO-66-NH₂ together with graphene, which is beneficial to the interfacial charge transfer and the separation efficiency of photogenerated electrons and holes in the MoS₂ QDs/UiO-66-NH₂/G composites. The electron of excited dye molecule transfer to the catalyst surface when the dye adsorbed by offset face-to-face orientation *via* π - π conjugation between EY and aromatic regions of the UiO-66-NH₂ and graphene [33]. It is reasonable to assume that the electron transfers from excited dye to UiO-66-NH₂ and graphene through the π - π interactions, and finally electron transfers to MoS₂ QDs [32]. This process efficiently improved the interfacial charge transfer and the separation efficiency of photogenerated charges, thus accounting for the H₂ evolution activity significantly enhanced under visible light irradiation.

3.6. Electrochemical analysis

The charge transfer of the samples was studied by the Nyquist plots of electrochemical impedance spectroscopy (EIS) in dark. As shown in Fig. 11A, the semicircular diameter of EY-MoS₂ QDs/UiO-66-NH₂/G is the smallest compared with those of dye sensitized samples, indicating the excellent conductivity of the catalyst and further accelerated the charge transfer after introduction of MoS₂ QDs and graphene. This phenomenon further proves the lower recombination rate of charges and fast interfacial electron transfer in EY-MoS₂ QDs/UiO-66-NH₂/G due to introduction of MoS₂ QDs and graphene, which is in agreement with the above PL results.

The transient photocurrent responses of dye sensitized UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs/UiO-66-NH₂, MoS₂ QDs/UiO-66-NH₂/G coated on FTO was investigated for several on – off cycles of intermittent irradiation. As shown in Fig. 11B, the MoS₂ QDs/UiO-66-NH₂/G composite shows the highest photocurrent intensity in the six samples, which is in accordance with the improved photocatalytic H₂ evolution activity, whereas the lowest photocurrent intensity can be observed in the EY-UiO-66-NH₂ sample. The spectra results additionally reveal the photocatalytic activity of the composite can be attributed to the synergistic effect of MoS₂ QDs and UiO-66-NH₂ together with



Scheme 1. Photocatalytic mechanism for H₂ production over EY sensitized MoS₂ QDs/UiO-66-NH₂/G under visible light irradiation.

graphene, which greatly improved the interfacial electron transfer from EY to MoS₂ QDs/UiO-66-NH₂/G. As a result, the photocatalytic H₂ evolution activity was enhanced. Due to the dye Eosin Y on the surface of FTO is dissolving in the electrolyte after a while, so lead to a higher dark current density over the high activity catalyst before measurement.

Furthermore, the electrochemical H₂ evolution activities of dye sensitized UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs/UiO-66-NH₂, MoS₂ QDs/UiO-66-NH₂/G electrodes were also investigated by the linear sweep voltammetry (LSV) technique. As shown in Fig. 11C, the cathodic current related to the reduction of water to H₂ on bare FTO electrode was extremely low even at high applied potentials. But dye sensitized FTO/EY-UiO-66-NH₂, FTO/MoS₂ QDs, FTO/UiO-66-NH₂/G, FTO/MoS₂ QDs/G, FTO/MoS₂ QDs/UiO-66-NH₂, FTO/MoS₂ QDs/UiO-66-NH₂/G electrodes showed an increased cathodic current at a similar potential range and the highest current density was observed for the FTO/MoS₂ QDs/UiO-66-NH₂/G electrode, which clearly indicating MoS₂ QDs/UiO-66-NH₂/G material was an excellent electrocatalyst that could efficiently catalyze the reduction of water to H₂.

3.7. The speculation of mechanism for H₂ evolution

Based on the above characterizations, the reaction process of photocatalysis H₂ evolution in EY-sensitized MoS₂ QDs/UiO-66-NH₂/G system can be depicted in Scheme 1. The high photocatalytic H₂ generation activity is attributed to the synergistic effect of the MoS₂ QDs and graphene together with UiO-66-NH₂. UiO-66-NH₂ has a large surface area of ~712.33 m² g⁻¹, well-ordered porous structures and channels, which is conducive to the dye absorption and electron transfer. When UiO-66-NH₂ grown on the graphene, which creating most active-sites, like microreactor in the porous structures and channels of MOF on the surface of graphene. MoS₂ QDs with much different exposed edges implanted on UiO-66-NH₂ or graphene is conducive to the electron transfer owing to the quantum confinement effect of MoS₂ QDs, which with graphene formation synergistic effect for electron transfer, thereby enhancing the photocatalytic H₂ evolution activity. Under visible light irradiation, the absorbed EY on the surface of UiO-66-NH₂/G absorbs light photons to form singlet excited state EY¹*, which subsequently produces the lowest-lying triplet excited state EY³* *via* an efficient intersystem crossing (ISC). Then, EY³* is reductively quenched by TEOA to produce EY^{•-} and oxidative donor (TEOA^{•+}) [29]. These EY^{•-} species preferentially transferred to the UiO-66-NH₂ and graphene, due to its electron transport characteristics, and then

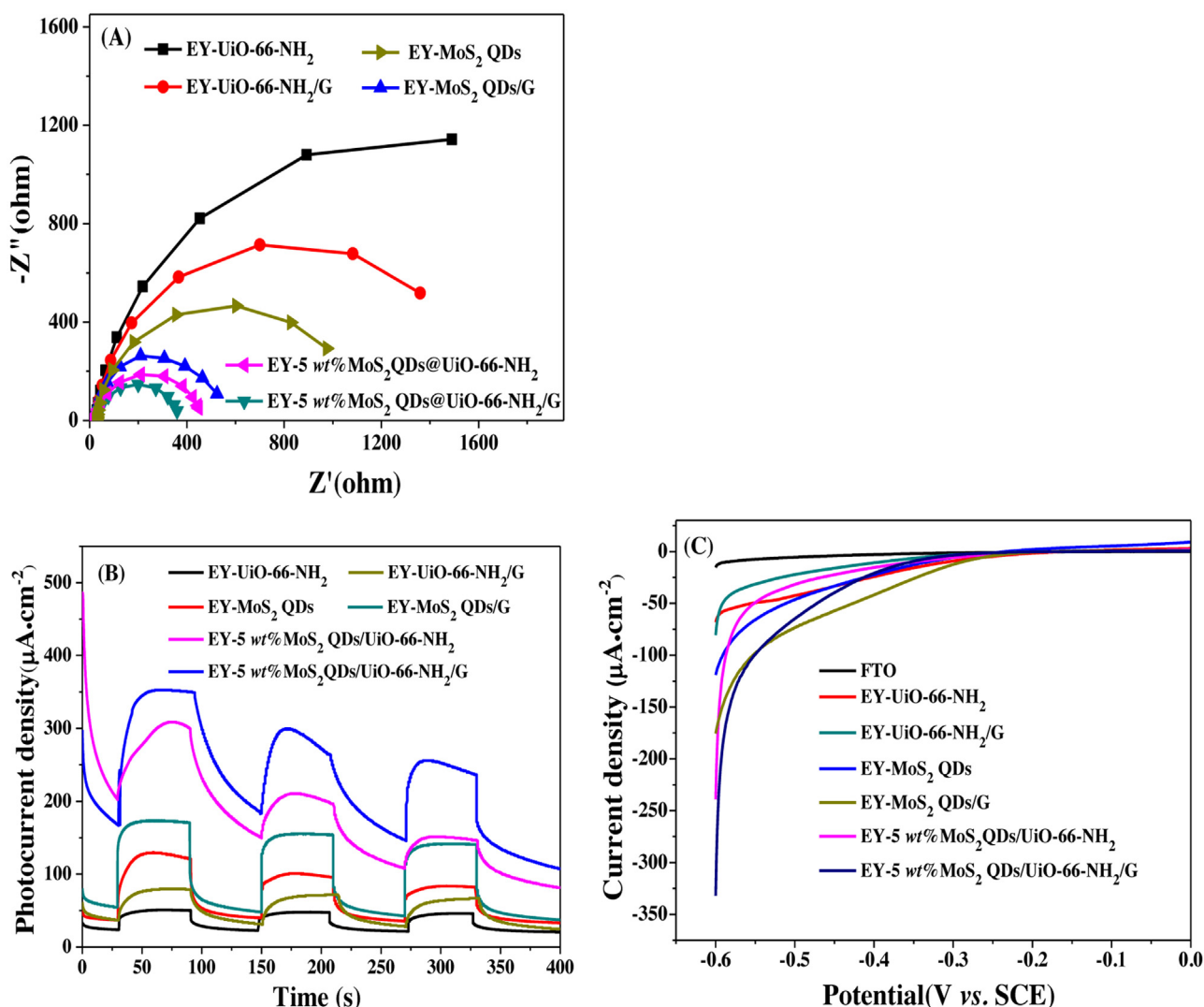


Fig. 11. (A) Nyquist plots of electrochemical impedance spectroscopy (EIS) and (B) transient photocurrent response for the EY-sensitized UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs@UiO-66-NH₂, MoS₂ QDs@UiO-66-NH₂/G coated on FTO in a mixed solution of 10 v/v% TEOA and Na₂SO₄ (0.1 mol L⁻¹) at pH 7 under visible light irradiation. (C) LSV curves of EY sensitized UiO-66-NH₂, MoS₂ QDs, UiO-66-NH₂/G, MoS₂ QDs/G, MoS₂ QDs@UiO-66-NH₂, MoS₂ QDs@UiO-66-NH₂/G coated on FTO in a mixed solution of 10 v/v% TEOA and Na₂SO₄ (0.1 mol L⁻¹) at pH 7. The scan rate was 1 mV s⁻¹.

transferred to the loaded MoS₂ QDs where the protons are mainly reduced to form molecular H₂. Simultaneously, the reduced state dye species get back to the ground state, accomplishing complete water reduction reaction. In addition, EY-sensitized MoS₂ QDs also can reduce H⁺ to produce H₂. UiO-66-NH₂ can function as an excellent dye adsorbent due to its porous structures and channel effect, and it can also act as an electron acceptor and transporter because of its channel confinement effect. Graphene also function as an excellent electron acceptor and transporter which with UiO-66-NH₂ synergistic efficiently prolong the lifetime of charge carriers and consequently improve the charge separation efficiency. Thus, the photocatalytic H₂ evolution activity of the MoS₂ QDs@UiO-66-NH₂/G was remarkably enhanced. It is therefore concluded that the MoS₂ QDs have great potential to replace noble metal as cocatalyst for photocatalytic hydrogen evolution.

4. Conclusions

In summary, a high active co-catalyst, MoS₂ QDs, anchored on UiO-66-NH₂/G was employed as catalysts for the photocatalytic activity toward hydrogen evolution from water with Eosin Y as

antenna molecule under visible light irradiation. The introduction of MoS₂ QDs efficiently improved photo-generated charge carriers and electron transfer and significantly enhanced the photocatalytic hydrogen evolution. The UiO-66-NH₂/G possessed high specific surface area (578.78 m² g⁻¹) which supported MoS₂ QDs formation synergistic catalytic effect and exhibited the excellent photocatalytic activity and stability for hydrogen evolution. A possible reaction mechanism of the MoS₂ QDs@UiO-66-NH₂/G was corroborated by photo-luminescence spectra, photo-electro-chemical characterizations and electro-chemical impedance spectra studies. Fluorescence studies shown that the charge separation and electrons transfer were more efficient by means of the introduction of MoS₂ QDs and graphene together with UiO-66-NH₂. The UiO-66-NH₂/G can not only contribute to the more efficiently absorb Eosin dye but also beneficial to efficiently transfer electrons due to the electron transport characteristics. Thus, the unusual catalytic activity arises from the synergistic effects between MoS₂ QDs and graphene together with UiO-66-NH₂, and an excellent photocatalytic activity for H₂ evolution was obtained over the dye-sensitized MoS₂ QDs@UiO-66-NH₂/G photocatalyst. The rate of H₂ evolution reached 62.12 μmol h⁻¹ over the EY-sensitized 5 wt%

MoS₂ QDs/UiO-66-NH₂/G irradiated under visible light irradiation ($\lambda \geq 420$ nm), and the apparent quantum efficiency (AQE) of 40.5% was achieved under 430 nm. MoS₂ QDs might be a promising alternative to replace noble-metal as cocatalyst for design new type of catalysts in photocatalysis proton reduction.

Acknowledgement

This work was financially supported by the Chinese National Natural Science Foundation (21603274, 21263001, 41663012 and 21433007).

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